Selective separation of some ecotoxic transition metal ions from aqueous solutions using immobilized macrocyclic material containing solid phase extraction system

Selective Separation of Some Ecotoxic Transition Metal Ions from Aqueous Solutions using Immobilized Macrocyclic Material Containing Solid Phase Extraction System

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Abstract

A simple flow-based method was developed for the simultaneous separation of certain transition metal ions (Co, Ni, Cu, Zn, Cd) from aqueous systems, which ions show ecotoxic effects when present at elevated concentrations. A silica-gel-bonded macrocycle system, commonly known as molecular recognition technology (MRT) gel, was used for solid phase extraction (SPE) of the target analytes. The collection behavior of the MRT-SPE system was studied based on pH. Fortified deionized water samples containing 250 μg L^{-1} of each of the elements were treated at the flow rate of 1 mL min–1. The collected analytes were then eluted by 3 M HNO_3 and analyzed using inductively coupled plasma spectrometry. Detection limits of the proposed technique were in the range of 0.004–0.040 μg L^{-1} for the studied metal ions. The validity of this separation technique was checked with spiked 'real' water samples, which produced satisfactory recoveries of 96–102%. The non-destructive nature and highly selective ion-extraction capability of the SPE material are the most important aspects of the proposed method and they are the main focus of this paper.

Keywords

Solid phase extraction, Molecular Recognition Technology, non-destructive, selective separation, aqueous system

1.0 Introduction

The behaviour and effects of transition metal ions (TMIs) in the aquatic environment are an important issue discussed among the environmental chemists and eco-toxicologists [1-6]. TMIs, at trace level, are readily dissolved and transported in water, and, as being ubiquitous, can act as a source of environmental pollution [6]. Some TMIs are biologically important; however, it is difficult to distinguish between their beneficial and harmful effects [7]. TMIs easily interact with aquatic organisms and they can act as a nutrient in small concentrations, while the ecotoxic effects may be observed at elevated concentrations [8, 9].

Various analytical techniques such as X-ray fluorescence [10], atomic fluorescence spectrometry [11], atomic absorption spectrophotometry [12, 13], inductively coupled plasma mass spectroscopy [14], inductively coupled plasma optical emission spectrometry (ICP-OES) [15, 16] are available for the determination of trace metals, with ICP-based techniques being the most commonly in use at the present times. Accurate analysis of TMIs in aqueous samples is difficult due to their complex formation and significant matrices, and because of their low sensitivity at trace level concentrations [17, 18]. Hence, separation/preconcentration steps combined with the analytical techniques are suggested to enhance the accuracy of results and analytical detection limits [7]. Some potential techniques proposed for separation and preconcentration of TMIs prior to the analytical measurements include co-precipitation [14, 19], membrane filtration [20], liquid-liquid extraction [21, 22], cloud point extraction [23-25], micro-extraction [26], and solid-phase extraction [17, 27, 28].

Solid phase extraction (SPE) is superior to the conventional extraction techniques [17, 29] due to its simplicity, rapidity, renewability and eco-safety. Analytical- or process-scale selective separation using SPE technique requires a material which has (i) highly selective affinity to the target analyte in the matrix range requiring separation, (ii) fast rate of analyte

extraction from the loaded sample solution followed by effortless elution with the suitable solvent, (iii) repeated usability and (iv) a wide range of accessibility [16, 30-34].

A number of SPE materials are available for the selective separation/preconcentration of TMIs (*e.g.* activated carbon [17], amberlite XAD resins [35], chromosorb resin [36], ambersorb resin [37], sodium dodecyl sulfate coated alumina [12], polyurethane foam [38], chitosan [39], molecular recognition technology (MRT) gel [15, 31]). In MRT, macrocycles covalently attached to the inert silica or polymeric support materials are used as the SPE material. Here, separation of the target analyte is performed based on the combination of size, configuration, electronic interaction, charge, wetting, and other factors [40]. The MRT-SPE materials are commercially available and they offer non-destructive, selective, and fast separation of the analyte of interest [15, 16, 31-33, 40].

In this work, a simple method for separation of Co, Ni, Cu, Zn and Cd from aqueous samples is proposed using a MRT-SPE system. HNO_3 was used as an eluent to recover the collected analytes in the MRT-SPE system, and the effluent was subjected to ICP-OES analysis for metal content evaluation. The parameters including sample pH, flow rate, eluent volume and concentration were optimized. To the best of our knowledge we report first such separation from aqueous solution with the application of MRT-SPE system. The technique has the potential to be used for both, enrichment as well as separation of TMIs from the natural samples and industrial waste solutions.

2.0 Experimental

2.1 Instruments

An SPS 5100 ICP-OES system (SII NanoTechnology Inc., Japan) composed of a radio frequency generator (40 MHz, 1.2 kW), a one-piece extended torch in the axial view mode, glass cyclonic spray chamber and sea spray glass concentric nebulizer was used. Argon gas

100 was used to maintain the plasma gas flow, auxiliary gas flow and nebulizer gas flow at 15.0,
101 1.50 and 0.75 L min^{-1}, respectively.

102 An automated computer-controlled robotic system, MetaPREP APS-1 (M&S Instruments,
103 Japan), was used for sample loading and treatment. A Navi F-52 pH meter (Horiba
104 Instruments, Japan) and a combination electrode were used for sample pH measurements.

105 ***2.2 Reagents and materials***

106 Single-element standard stock solutions (1000 mg L^{-1}) from Plasma CAL, SCP Science,
107 Canada, were used to prepare the working standards in the range of mg L^{-1} to µg L^{-1} *via*
108 dilution by weight. Ultrapure water (18.3 MΩ cm resistivity), referred to as ultrapure water
109 hereafter, prepared by an Elix 3/Milli-Q Element system (Nihon Millipore, Japan) was used
110 throughout the study. Ultrapure reagent grade HNO_3 (PlasmaPURE Plus, SCP Science,
111 Canada), was diluted with the ultrapure water to the desired concentrations, and used in the
112 washing and elution steps. Ammonium acetate solution was prepared using acetic acid and
113 ammonia water, as purchased from Kanto Chemicals, Japan.

114 The ion-selective MRT-SPE material, AnaLig TE-05, was purchased from GL Sciences
115 Inc., Japan with the following specifications: (a) mesh size – 60 to 100; (b) density – 0.4 g
116 mL^{-1}; (c) operational pH range – up to 10.5; and (d) binding capacity – 0.1 to 0.3 mmol g^{-1}.

117 Cations added as NaCl, KCl, $CaCl_2$, $MgCl_2$ and the Na-salt of anions (Cl^-, NO_3^-, PO_4^{3-},
118 SO_4^{2-}) (Nacalai Tesque, Japan) were used to study the effect of matrix ions. Working
119 solutions were prepared in H_2O matrix with pH maintained at 7. The final solutions were
120 allowed to equilibrate for 24 h before use.

121 Synthetic multi-element waste solution containing 250 µg L^{-1} of several elements,
122 prepared from the single element metal standard solutions (1000 mg L^{-1}) and a multi-element
123 standard solution XSTC-13 (10 mg L^{-1}, Spex CertiPrep Inc., NJ, USA) *via* dilution by weight
124 and *via* mixing, was used for the recovery test. Fortified samples of the 'real' waters (tap and

125 river water), were filtered using the cellulose membrane filter of 0.45 μm pore size (Advantec,
126 Japan) prior to analysis.

127 ***2.3 Cleaning***

128 Low-density polyethylene laboratory wares (Nalge, USA) were soaked in an alkaline
129 detergent (Scat 20X-PF, Nacalai Tesque, Japan) overnight to initiate the process of cleaning.
130 The further steps included rinsing with ultrapure water followed by soaking in 4 M HCl
131 overnight, and rinsing again with ultrapure water. The procedure described by Sohrin *et al*.
132 [41] was followed, in order to clean the perfluoroalkoxy tubes and micropipette tips
133 (Nichiryo, Japan).

134 ***2.4 Separation process***

135 A mini-column (3 mL) containing the SPE material was used to evaluate the separation
136 process in five steps: rinsing, conditioning, collection, washing, and elution (Fig. 1). The
137 MRT-SPE column was rinsed with 3 M HNO_3 (10 mL) and ultrapure water (10 mL),
138 followed by conditioning with the acid or buffer solutions of appropriate pH. Metal ions were
139 collected from the sample solution after passing through the SPE column. The column was
140 then washed with 10 mL of ultrapure water. In the next step, the analytes 'captured' in the
141 MRT-SPE column were eluted using 3 M HNO_3 with subsequent ICP-OES determination.

142 **3.0 Results and discussion**

143 ***3.1 Effect of pH***

144 Collection behaviour of the metal ions (Co, Ni, Cu, Zn or Cd) in the TE-05 MRT-SPE
145 column was studied as a function of pH (Fig. 2). HNO_3 (0.001–1 M) and ammonium acetate
146 solution (0.2 M) were used to adjust the sample pH in the range of 1 to 9. Recovery
147 efficiencies ≥ 95% for the studied metal ions were observed at a range of pH or at multiple
148 pHs: Co (4–8), Ni (6–9), Cu (1–9), Zn (7 and 9), Cd (4–8). However, at pH 7.0, nearly

149 quantitative collection (%) of all the target analytes was observed (Co, 103±3.56; Ni,
150 101±4.46; Cu, 103±3.66; Zn, 95.2±3.70; Cd, 98.4±3.12). Hence, a sample pH at 7 was kept
151 for further experiments.

152 ***3.2 Effect of flow rate***

153 Sample loading or elution flow rate have a significant consequence on the performance of
154 any SPE material during the process of collection or elution. Therefore, at optimum
155 conditions, the effect of sample loading and elution flow rates on the behaviour of TE-05
156 column was examined in the range of 1 to 5 and 1 to 4 mL min^{-1} respectively (Fig. 3).
157 Maximum rate (%) of collection (Co, 101±1.99; Ni, 100±2.02; Cu, 101±2.22; Zn, 102±5.85;
158 Cd, 102±2.67) and elution (Co, 102±1.97; Ni, 102±4.00; Cu, 102±2.20; Zn, 101±2.86; Cd,
159 102±2.64) of the target analytes on the MRT-SPE column was observed at the flow rate of 1
160 mL min^{-1}. A gradual decrease in the collection or elution efficiency with the increase in the
161 flow rates was observed indicating, respectively, the constant collection or regeneration
162 capability of the MRT-SPE column at the initial period of loading or elution. Based on the
163 observation, a sample loading or elution flow rate of 1 mL min^{-1} was maintained during the
164 subsequent experiments.

165 ***3.3 Effect of eluent concentration and volume***

166 A high enrichment factor can be achieved during the separation process, if the eluent
167 possesses the capacity to recover the analyte with a minimum volume without affecting the
168 precise determination of the analyte [42]. Fortified aqueous samples, containing 250 µg L^{-1}
169 the target analytes (Co, Ni, Cu, Zn or Cd), were passed through the MRT-SPE column,
170 followed by elution using 0.5–3 M HNO_3 with succeeding ICP-OES analysis (Fig. 4a). The
171 maximum recovery (%) of analytes was accomplished at ≥ 2.0 M HNO_3. The requisite eluent
172 volume for complete elution of the 'captured' analytes from the MRT-SPE system was
173 studied (Fig. 4b). A series of elution experiments with eluent volumes in the range of 2 to 7

mL produced discrete patterns in the elution behaviour for different analytes. Maximum recovery of the target analytes was achieved with the eluent volume of ≥ 4 mL. Hence, 4 mL of 3 M HNO_3 was preferred for the elution steps in the subsequent experiments.

3.4 Effect of matrix ions

In order to investigate determination and selective separation of Co, Ni, Cu, Zn, or Cd ions from their binary mixtures with diverse matrix ions, an aliquot of aqueous solutions (100 mL) containing 250 μg L^{-1} of the target analytes and other ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) at the molar ratio of 1 to 100 was taken and treated under the optimal conditions. Satisfactory recovery (%) of the analytes (Co, 101±3.46; Ni, 100±4.46; Cu, 102±4.69; Zn, 95.4±2.72; Cd, 97.4±4.12) from aqueous matrix was observed. An error of less than 5% was considered to be within the range of experimental error. The results indicate that there is a preferential uptake of the target ions relative to matrix ions, and it is assumed that in the analysis of aqueous samples, the separation efficiency is not affected by the presence of a high content of matrix ions.

3.5 Analytical characteristics

Aqueous samples fortified with TMIs (Co, Ni, Cu, Zn, Cd) were treated with TE-05 MRT-SPE column, and the concentrations of the target analytes in the treated samples was measured with ICP-OES. Linear calibration curves were obtained for Co, Ni, Cu, Zn and Cd concentrations from 1 to 20 μg L^{-1} with the respective correlation coefficients of 0.9785, 0.9755, 0.9955, 0.9914 and 0.9908 under optimum conditions. The method detection limits, as calculated from three times higher standard deviation (n = 15) of the blank, was 0.006, 0.040, 0.006, 0.009 and 0.004 μg L^{-1}. The precision of the method for aqueous standards was evaluated by analyzing 10 replicates with the analyte concentration of 10 μg L^{-1}, which gave relative standard deviations of 1.4, 2.2, 1.9, 2.7 and 2.3%, respectively, for Co, Ni, Cu, Zn and Cd.

3.6 Retention capacity and reuse of the SPE column

Retention capacity, which is an indication of the stability of the MRT-SPE column during the separation process, can be calculated from the analyte concentration and breakthrough volume (the volume of sample that causes the target analyte to be eluted from the SPE columns) [43]. Sample solutions spiked with metal ions were passed through the MRT-SPE column, eluted and subjected to ICP-OES analysis. The retention capacity of the MRT-SPE at pH 7 was 0.26±0.08–0.32±0.11 mmol g^{-1}. The regeneration ability of the MRT-SPE column was investigated, and it was observed that the column could be reused for more than 100 loading and elution cycles without the loss of analytical performance.

3.7 Application of the separation process

3.7.1 Recovery of analytes from synthetic metal-waste solution

Synthetic metal-mixture in aqueous matrix (4 mL) containing 250 µg L^{-1} each of 32 different elements (Li, Be, B, Na, Mg, Al, K, Sc, V, Cr, Mn, Fe, Ga, Sr, Zr, Nb, Mo, Rh, Pd, Ag, Sn, Ba, Hf, Ta, W, Pt, Hg, Tl, Pb, Bi, Th, U) and 5 target analytes was loaded onto MRT-SPE column followed by elution with 3 M HNO_3 (4 mL). The recoveries (%) of Co, Ni, Cu, Zn and Cd from the metal-matrix at pH 7 were found to be 101±2.72, 100±3.94, 99.7±4.40, 96.4±1.83, and 98.2±3.85, respectively, after treatment with TE-05 at optimum conditions.

3.7.2 Recovery of analytes from spiked real samples

The proposed separation process was applied for the determination of Co, Ni, Cu, Zn and Cd in local natural water samples (tap and river water) spiked with known amounts of the target analytes (Table 1). The recoveries of the target ions from the fortified solutions were in the range of 95.8±1.64 to 102±3.76%.

3.8 Comparison of MRT-SPE with other SPE-systems

Characteristics of the MRT-SPE and some other SPE-systems are compared in Table 2. The data for other SPE-systems is available in literature [17, 37, 38, 44, 45] and carefully

224 selected based on the number of metals covered during the separation process corresponding
225 to our study. Most of the SPE systems have been used for column separation of trace metals
226 at the pH of 6.0–7.5. The advantages of the MRT-SPE system include higher regeneration
227 ability in comparison with other SPE materials. SPE systems with macrocycles attached onto
228 solid supports allow selective separation of analytes from matrix facilitating the repeated use
229 of the macrocycles [46-48]. Hence, superior regeneration ability of the MRT-SPE system is
230 expected. The initial high cost of synthesis can be amortized over time due to the repeated
231 usability. The limits of detection achieved by the present method are comparable to those
232 cited in Table 2. Another advantage of MRT-SPE is the one-step separation process which is
233 easy to perform and enhances the reproducibility of the separation process

234 **4.0 Conclusions**

235 AnaLig TE-05, an immobilized macrocyclic compound containing SPE system popularly
236 known as MRT gel, was used for the separation of Co, Ni, Cu, Zn and Cd from aqueous
237 solutions followed by ICP-OES analysis. Quantitative separation of the target analytes was
238 performed at the following optimized conditions: a) pH: 7, b) sample loading/elution flow
239 rate: 1 mL min^{-1} and c) eluent: 3 M HNO_3. Selective separation of the desired ions was
240 achieved with the MRT-SPE column in the presence of several competing ions. The column
241 regeneration process is simple and the column can be used for several operations without a
242 substantial alternation in the analytical performance. Therefore, TE-05 MRT-SPE system
243 provides an excellent option for the selective separation of Co, Ni, Cu, Zn or Cd ions from
244 the aqueous matrix with high metal content, or for the separation/preconcentration of the
245 mentioned ions from natural water systems prior to the analytical determination.
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339 Table 1. Determination of analytes in the spiked real water samples (n = 5)

Analytes	Tap water			River water		
	Added ($\mu g\ L^{-1}$)	Found ($\mu g\ L^{-1}$)	Recovery (%)	Added ($\mu g\ L^{-1}$)	Found ($\mu g\ L^{-1}$)	Recovery (%)
Co	0	0.11±0.02	–	0	0.10±0.01	–
	100	102±3.43	102±3.38	100	102±3.39	102±3.76
Ni	0	1.33±0.04	–	0	0.95±0.05	–
	100	102±3.81	100±3.78	100	101±3.84	99.9±1.85
Cu	0	1.24±0.13	–	0	0.75±0.03	–
	100	101±2.73	99.4±3.75	100	101±2.69	101±2.05
Zn	0	4.02±0.26	–	0	1.43±0.11	–
	100	102±2.39	98.4±2.52	100	97.2±1.61	95.8±1.64
Cd	0	0.04±0.02	–	0	0.05±0.01	–
	100	96.8±3.31	96.8±4.24	100	98.9±3.17	98.9±3.04

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359 Table 2. Comparative data of the studied ions on different solid phase extraction (SPE)

360 systems

Elements	Sample	SPE system [a]	Detector [b]	LOD [c] (μg L^{-1})	pH	Reusability (cycle)	Ref.
Co, Ni, Cu, Zn, Cd	Tap and river water	Silica gel/macrocycle	ICP-OES	0.004–0.040	7	~100	This work
Co, Ni, Cu, Cd, (and Pb, Fe)	Sea water and natural waters	Poly(MAA-*co*-TMPTMA)	FAAS, GFAAS	0.005–0.02	7.5	50	[44]
Co, Ni, Cu, Cd, (and Pb, Cr)	Tap water, bottled mineral water	Ambersorb 563/ PAN	FAAS	0.21–0.67	9	50	[37]
Co, Cu, Cd, Zn, (and Pb, Cr)	Agriculture product, hair, milk, waste and river water samples	SDS-PVC/ BHABDI	FAAS	0.27 – 0.39	7	–	[45]
Co, Ni, Cu, (and Pb)	Natural water samples, leaves of spinach and liver samples	Activated carbon /DHMP	FAAS.	2.9 –8.4	6	–	[17]
Cu, Zn, Cd, (and Pb)	Drinking water	Amberlite XAD-2/ HPAPyr	FAAS	0.9 –3.3	7	17	[28]

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362 [a] Silica gel/macrocycle: macrocyclic material immobilized on silica gel; poly(MAA-*co*-TMPTMA): a microsphere polymer gel synthesized
363 using methacrylic acid (MAA) as a monomer and trimethylolpropane trimethacrylate (TMPTMA) as a crosslinking agent; ambersorb 563/
364 PAN: 1-(2-pyridylazo) 2-naphtol (PAN) impregnated ambersorb 563 resin; SDS-PVC/BHABDI: sodium dodecyl sulfate (SDS)-coated
365 poly vinyl chloride (PVC) modified with bis(2-hydroxyacetophenone)-1,4-butanediimine (BHABDI) ligand; activated carbon/DHMP:
366 4,6-dihydroxy-2-mercaptopyrimidine (DHMP) loaded on activated carbon; amberlite XAD-2/HPAPyr: amberlite XAD-2 functionalized
367 with 4′-(2-hydroxyphenylazo)-3′-methyl-1′-phenyl-2′-pyrazolin-5′-one (HPAPyr).
368 [b] ICP-OES: inductively coupled plasma optical emission spectrometry; FAAS: flame atomic absorption spectrometry; GFAAS: Graphite
369 furnace atomic absorption spectrometry
370 [c] LOD: limit of detection
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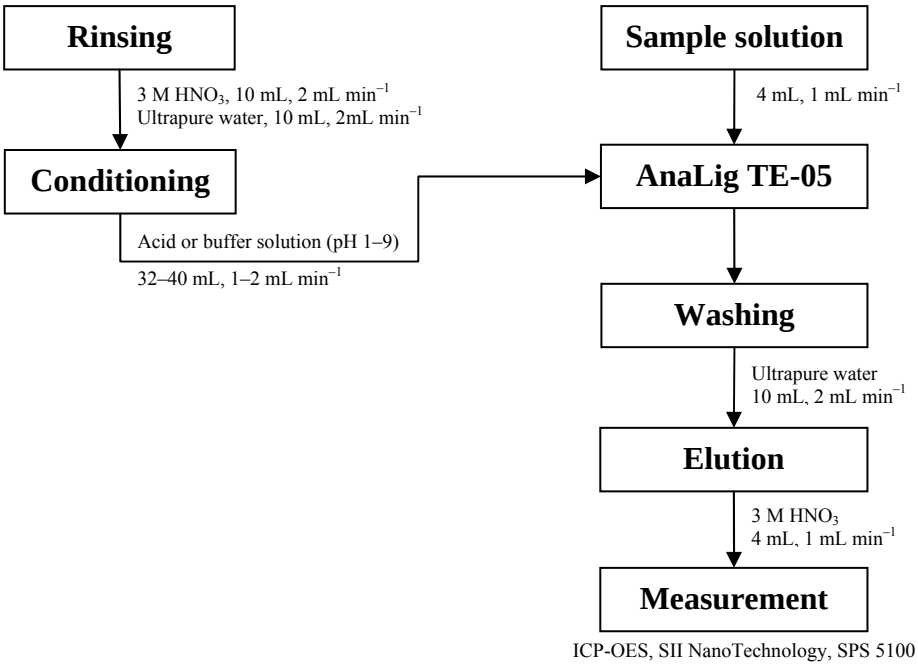
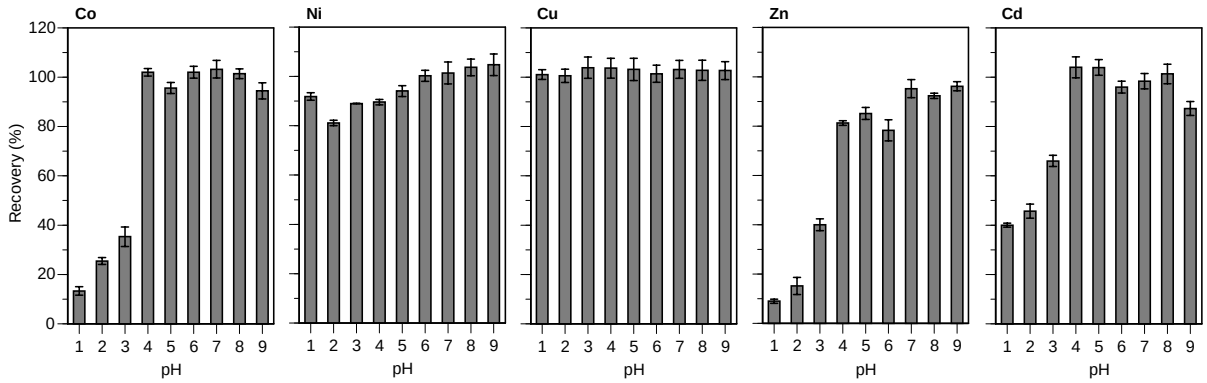


Figure 1: Schematic diagram of the experimental setup



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395 Figure 2: Effect of pH on the collection behavior of the MRT-SPE column. Sample solution:

396 250 μg L^{-1} (Co, Ni, Cu, Zn or Cd), pH: 1−9, volume: 4 mL, loading flow rate: 1 mL min^{-1},

397 eluent: 3 M HNO_3, eluent volume: 4 mL, elution flow rate: 1 mL min^{-1} (n = 3).

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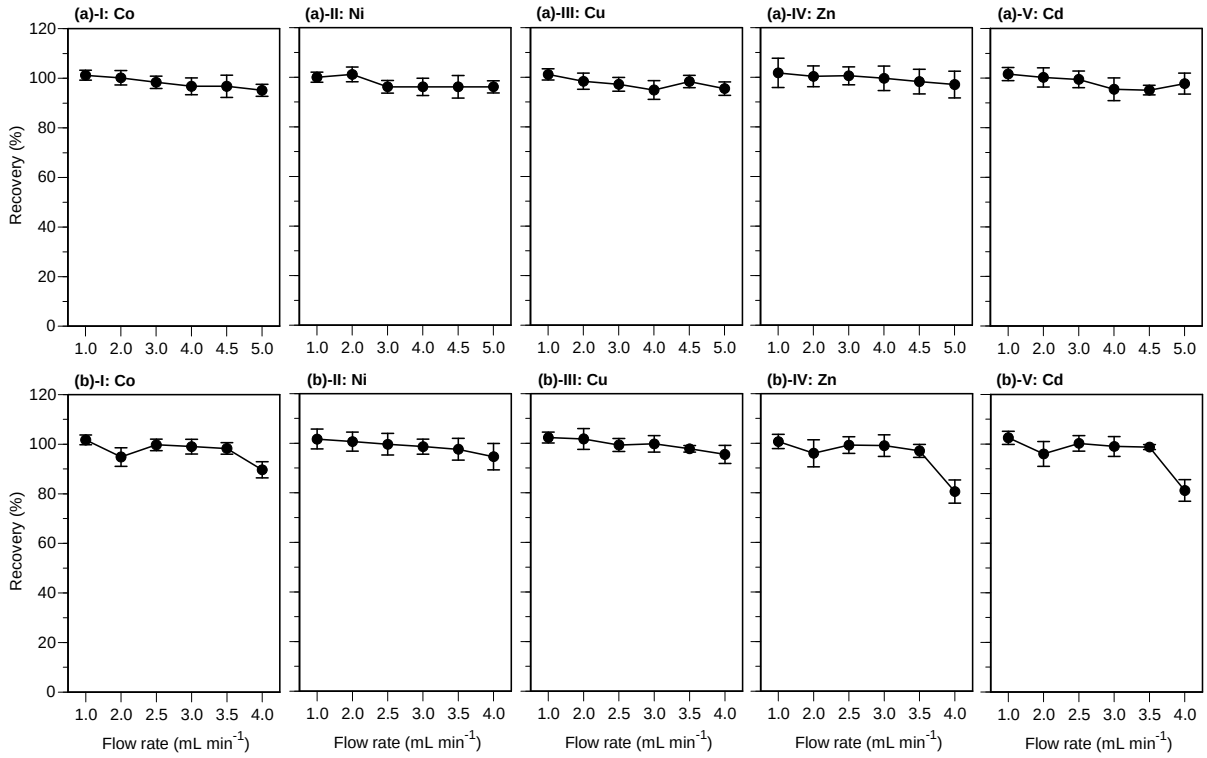

Figure 3: Effect of (a) sample loading and (b) elution flow rates on the collection behavior of the MRT-SPE column. Sample solution: 250 µg L^{-1} (Co, Ni, Cu, Zn or Cd), pH: 7, volume: 4 mL, loading flow rate: 1–5 mL min^{-1}, eluent: 3 M HNO_3, eluent volume: 4 mL, elution flow rate: 1–4 mL min^{-1} (n = 3).

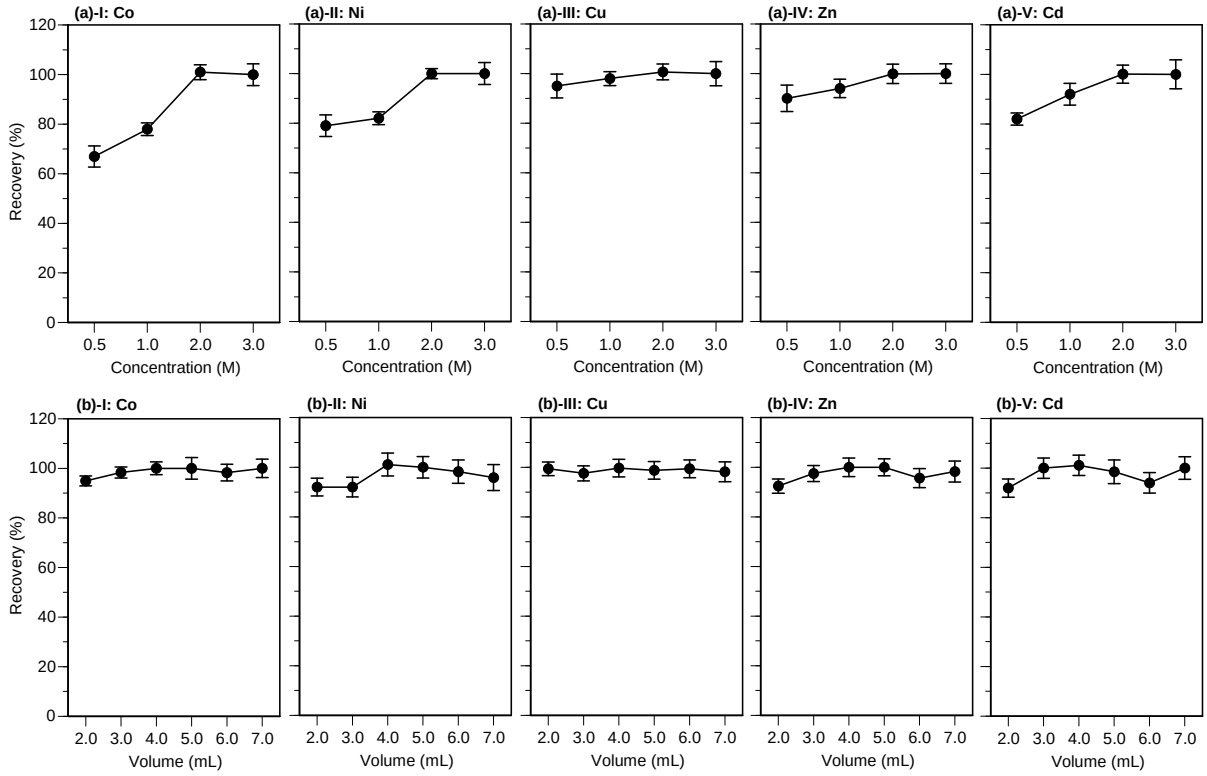

Figure 4: Effect of (a) eluent concentration and (b) eluent volume on the collection behavior of the MRT-SPE column. Sample solution: 250 μg L^{-1} (Co, Ni, Cu, Zn or Cd), pH: 7, volume: 4 mL, loading flow rate: 1 mL min^{-1}, eluent: 0.5−3 M HNO_3, eluent volume: 2−7 mL, elution flow rate: 1 mL min^{-1} (n = 3).